Indian J. Phys. **51B**, 383-387 (1977)

Correlation energy in two electron atomic systems

P. K. MUKHERJEE

Department of Physics, University of Burdwan, Burdwan, West Bengal

H. P. ROY

Department of Physics, University of Jadavpur, Jadavpur, Calcutta-700032

AND

A. GUPTA

Saha Institute of Nuclear Physics, Calcutta-700009

In this paper a simplified method is presented to calculate the radial and angular correlation energy in two electron atomic systems in their ground states. The conventional Hartree-Fock (HF) method, though extensively used for handling many electron systems, does not yield accurate energy of the system and the evaluation of correlation energy of the system, has been the subject of interest for quite a long time. Various methods such as the configuration interaction (CI) approach or many body perturbation theory (MBPT) have been applied to estimate this energy. All these calculations are quite laborious and require large computer time particularly when the atomic number of the system increases. Here we adopt a method which takes care of the interacting system properly by working in terms of single particle basis set. Our approach is equivalent to a full CI calculation but differs from a CI or MBPT calculation in the manner that we take a suitable Slater type basis for the description of our system whereas in a CI or MBPT calculation a complete set of eigenstates of a suitable model Hamiltonian is necessary. Moreover our method takes comparatively less computer time than a full CI calculation. In our method the total wavefunction is written as a linear combination of two particle basic functions. Each basis function is a product of two one electron functions. This function gives correlated description of the system. Angular correlation is obtained by symmetrising the wave function with appropriate projection operators. In our calculation only s and p type correlation is included. Energies of He sequence upto C^{4+} are evaluated including that of H^- ion. The electron affinity of H atom obtained by this procedure is very satisfactory. For the case of H we obtained 97% correlation energy by our procedure For H to C^{4+} about 90% of the correlation energy is accounted for.

1. Introduction

In the present paper a simple and straightforward method is presented to calculate the radial and angular correlation energy in two electron atomic systems. The conventional way of treating a many particle system is to construct a wavefunction formed out of antisymmetrised product of one particle functions. A single determinantal approach is usually followed. This approach called the Hartree-Fock (HF)[1,2] method is very suitable for handling such systems and is extensively used in atomic and nuclear calculations. However this procedure does not yield the correct energy of the system and the quantity

$$E_{Corr} = E_{NR} - E_{HF}$$

is referred to as the correlation energy of the system. E_{NR} is the non-relativistic energy and E_{HF} is the Hartree Fock energy. With increase of atomic number E_{Corr} increases and gives a significant contribution to the total energy of the system.

This difference of energy has been estimated by various methods like the configuration interaction (CI)[3,4,5] or many body perturbation theory (MBPT)[6]. However, in these calculations the labour involved and computation time required increases rapidly as the atomic number of the system increases. In this paper we adopt a method which takes care of the interacting system properly by working in terms of single particle basis set. The method has been adopted by Mukherji[7] where only radial correlation in such systems has been considered.

The present procedure differs from a CI or MBPT calculation in the manner that we take a suitable Slater type basis for the description of our system whereas in a CI or MBPT calculation the starting requirement is to have a complete set of eigenstates of a suitable model Hamiltonian. However, ultimately our procedure is equivalent to a full CI calculation with a given basis set.

2. Theory

The non-relativistic Hamiltonian of a two particle system with nuclear charge Z is given by (in a.u.)

$$H = \sum_{i=1}^{2} \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \frac{1}{r_{12}} \tag{1}$$

Our correlated description of the wavefunction of the system is given by an antisymmetrised product of a space and a spin part. The ground state function of such system is given by

$$\Psi(1,2) = \Phi(1,2)\ \chi(1,2) \tag{2}$$

where

$$\chi(1,2) \quad \frac{1}{\sqrt{2}} \left[\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1) \right] \tag{3}$$

is the spin part and $\Phi(1,2)$ is the space part, which we asume to be of the form

$$\Phi(1,2) = \tfrac{1}{2} \sum_{ij} C_{ij} \quad \xi_{ij} \quad (1,2) \tag{4}$$

where the C_{ij} 's are unknown parameters with the restriction $C_{ij} = C_{ji}$ to satisfy Pauli principle and ξ_{ij} (1,2) is a symmetric function formed out of atomic orbitals.

$$\xi_{ij} \quad (1,2) = \psi_i(1)\,\psi_j \quad (2) + \psi_i(2)\,\psi_j \quad (1) \tag{5}$$

where ψ_i 's are the single particle basis states. Obviously there are $n(n+1)/2$ number of independent C_{ij} 's if the individual one particle functions are described by a linear combination of n Slater type orbitals.

The function described by eqn. (4) is an eigenstate of L^2 and L_z operator. This can be easily done by appropriate projection operators.[5] In the present case we consider all the radial and a part of the angular correlation (p type) to describe the ground ^1S state of two electron systems. Hence the summation of i, j runs over all the s and p type basis states. The total energy is given by

$$E = \frac{<\Psi(1,2) \mid H \mid \Psi(1,2)>}{<\Psi(1,2) \mid \Psi(1,2)>} \tag{6}$$

and is obtained by solving the equation

$$HC = SCE \tag{7}$$

where S is the overlap matrix whose ij th element is

$$S_{ij} = <\psi_i \mid \psi_j>$$

Our correlated description of the system has the advantage that all basic integrals will be over single particle functions which usually appear in a HF calculation, The energy eigenvalue equation reduces to a set of simultaneous linear equations in the parameters and may be obtained in a single diagonalisation procedure.

3. Results

The correlation energy of two electron ions from H^- to C^{4+} in the ground ^1S state has been calculated. The energy values are listed in table 1. For

Table 1. Ground state correlation energy of two electron ions

Ion	E_{HF} [a] (a.u.)	E_0 Present calculation (a.u)	E_{NR} [b] (a.u.)	E Weiss[c] (a.u)	$E^{cal}_{corr.}$ (E_0-E_{HF}) (a.u.)	$E^{Exact}_{corr.}$ $(E_{NR}-E_{HF})$ (a.u.)	$\frac{E^{cal}_{corr}}{E^{Exact}_{corr.}}+100$
H^-	− 0.4881	− 0.52640	− 0.52775	−0.52647	−0.03830	−0.03965	96.6
He	− 2.86168	− 2.90014	− 2.90372	−2.90039	−0.03846	−0.04204	91.5
Li^+	− 7.23641	− 7.27547	− 7.2799,	−7.27575	−0.03906	−0.04250	89.8
Be^{2+}	−13.61126	−13.65052	−13 65557		−0.03926	−0.04431	88.6
B^{3+}	−21.98619	−22.02550	−22 03097		−0.03931	−0.04478	87.8
C^{4+}	−32.36115	−32.40026	−32.40625		−0.03911	−0.04510	86.7

[a] Taken from Clementi : Reference2

[b] Calculated by Pekeris : Reference 5.

[c] Values obtained by taking s and p correlations only : Reference 4.

comparison the energy values obtained from very accurate theoretical calculations[5] are also listed. Here four parameter Slater type representation for each of s and p orbitals are used. The exponents of the s orbitals for the systems He to C^{4+} are those of Clementi[2] and are optimized and for H^- we used the exponents of Mukherji[7]. For the case of p orbitals for all ions the exponents are chosen from physical considerations. This depends upon the type of p mixing we are considering for our representation of the one particle function.

The electron affinity of H as obtained by us is -0.0264 (a.u) which is a considerable improvement over the value −0.0133 (a.u.) obtained by Goddard[9] and −0.0133 (a.u.) obtained by Shull and Lowdin[10], all of them, howevr, include only radial correlation. The radially correlated value obtained by Mukherji[7] is −0.0143 (a.u). It shows that inclusion of angular correlation yields a substantially better result.

The ground state energy of He obtained by us is −2.90014 compared to −2.90039 obtained by Weiss[4] using 35 configurations in the wavefunction. This indicates that reasonable accuracy is obtained by our procedure with only a few parameters. The limit with p type mixing is -2.90042 (a.u.). For other ions table 1 shows in all cases our results agree well with the extensive calculations of Pekeris[5] and Weiss[4]. We are presently trying to see the convergence of our results by increasing the number of parameters. The results will be reported in due course.

ACKNOWLEDGMENTS

We are thankful to Professor A. Mukherji for illuminating discussions. One of the authors (P.K M) is grateful to Professor R. L. Sengupta, Head of the Department of Physics, University of Burdwan for allowing him the necessary research facilities.

REFERENCES

(1) D. R. Hartree. *The Calculation of Atomic Structures*. John Wiley and Sons, New York (1957).
(2) E. Clementi, *Tables of Atomic Functions*, IBM. Res Suppl (1965)
(3) J. C. Slater, *Quantum Theory of Atomic Structures*, Vol 2. McGraw-Hill, New York (1960).
(4) A. W. Weiss, Phys. Rev. **122**, 1826 (1961)
(5) C. L. Pekeris, Phys. Rev. **112**, 1649 (1958) ;
——— ibid. **115**, 1216 (1959).
(6) H. P. Kelly, Adv. Chem Phys., **14**, 129 (1969)
(7) A. Mukherji, Pramana, **2**, 54 (1974)
(8) Per Olov Lowdin, Rev. Mod. Phys. **36**, 966 (1964)
(9) W. A. Goddard, Phys. Rev **172**, 172 (1968).
(10) H. Shull and P. O. Lowdin, J. Chem Phys., **25**, 1039 (1956) ;
——— ibid, **30**, 617 (1959).